# NEW ATMOSPHERIC PLASMA AND PHOTOGRAFTING APPROACH FOR PERMANENT SURFACE TENSION AND COATING ADHESION

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**Abstract**
Flexible packaging comprised of polyolefins such as polypropylene have low levels of polar functional groups on the surface and have poor wettability and adhesion properties, making it difficult to apply other functional layers such as dyes, inks, adhesives and coatings. To enhance surface polarity, surface treatments such as flame, corona or plasma can be applied to improve wettability and adhesion. Plasma can specifically be used as a preparatory treatment for the photografting approach recommended in this paper to achieve high stability in treatment and permanent changes to the surface.

**Introduction**
To improve wettability and therefore adhesion, several physical treatments such as corona are usually applied on the surface, with a final effect of introducing polar groups and enhancing surface energy. However, these treatments are not stable and the resulting surface modification is uneven, showing variations during printing or coating processes. Moreover the improved adhesion of the functional layers is due to a purely physical interaction or to the formation of weak bonds. For these reasons, adhesion is weak and has low thermal and chemical resistance.

Atmospheric plasma glow discharge technology has advanced within the converting industry to become an exceptionally effective discharge treatment process which homogenously modifies surface chemistry to increase the bonding of interfaces such as dyes, inks, adhesives and coatings to three-dimensional surfaces such as polypropylene parts. Plasma treatment has significantly greater longevity than corona discharges, offers extraordinary longevity compared to corona, but is not permanent in nature. The introduction of an innovative photografting approach which delivers a proprietary molecule to a web surface prepared by atmospheric plasma treatment offers a potentially dynamic method of improving adhesion of inks, coatings and adhesives on flexible packaging substrates. This paper seeks to describe a methodology for utilizing these technologies to introduce processing improvements for flexible packaging.

**Principles of Atmospheric Plasma and Photografting Techniques**
Plasma processing of materials has been a vital industrial technology in many areas including electronics, aerospace, automotive, and biomedical industries. This is because of the unparalleled capability of plasmas for production of chemically reactive species at a low gas temperature while maintaining high uniform reaction rates over relatively large areas. In the past, the majority of plasma processing has been done at low pressure in a vacuum chamber and viewed as a necessary processing requirement. In principle and practice, however, atmospheric pressure plasmas provide a critical advantage over widely used low pressure plasmas as they do not require expensive and complicated vacuum systems. Without a vacuum system, the cost of materials processing are reduced substantially and materials issues related to vacuum compatibility are not of concern. Therefore, the use of atmospheric pressure plasmas is beginning to greatly expand the current scope of materials processing. Over the past few years, roll-to-roll atmospheric pressure plasma discharge systems have been developed for operation at commercial speeds. These systems produce glow discharges with a low gas temperature, typically below 300 °C, and provide efficient reaction rates for deposition over increasingly large surface areas.

Although there are different kinds of atmospheric pressure discharges, the most commonly used on industrial scale is the dielectric barrier discharge (DBD). A DBD is a non-thermal RF fourth-state-of-mater plasma with a gas discharge maintained between electrodes separated by at least one dielectric barrier. Atmospheric pressure DBDs usually consist of a multitude of transient micro-discharges of very short duration (several 10 ns), with diameters of about 0.1 mm and mean electron energies of typically 1-10 eV. Within these micro-discharges the gas is excited, ionized and dissociated, and highly reactive species are formed without a significant increase of the average gas temperature. Documented advantages for atmospheric plasma discharge treatments of two dimensional web-based materials are rooted in observations that ion bombardment physically and chemically removes oxides and reducible compounds from surfaces, with many contaminations vaporized. In addition, gas molecules are accelerated to an excited state,

releasing active chemical-free radicals and UV energy. Free radicals activate chemical reactions on surfaces, inducing intermolecular cross-linking. When compared to corona discharges, atmospheric plasmas produce significantly more homogeneous and uniform surface activation across material surfaces, increase the micro-roughness of surfaces, with introductions of active species. Atmospheric plasma power densities are not high enough to damage polymeric materials.

The principle for using a unique photografting technique for three dimensional surfaces initially requires the surface to be activated through physical pretreatment (suggested to be by atmospheric plasma in this paper). A proprietary liquid solution (solvent or water based) is applied after surface pre-treatment in amounts of 1g/m$^2$. It is applied to surfaces using a coating unit, and then the carrier liquid is removed by evaporation. A reactive photoinitiator is then grafted onto the surface by UV light exposure. Anchoring of the photoinitiator to the three dimensional surface ensures practically unlimited storage stability, as the surface tension assumes permanence.

It is the chemical/physical properties of the photoinitiator which supports the enhancement of the surface tension of the treated polymer substrate, thereby improving wettability. Moreover, grafting the photoinitiator onto the surface prevents it from migrating into the polymer mass. For this reason, the treatment has practically unlimited storage stability, provided exposure to UV light is avoided. The photoinitiator grafted from the carrier solution reacts during polymerization, forming a chemical bond between the interface (dye, ink, etc.) and three-dimensional part surface.

The proposed advantage of the plasma-photografting approach lies primarily in the matching of the homogenous surface treatment of polymeric surfaces using atmospheric plasma glow discharge technology with the uniformity of a photografting solution coated over structure surfaces. Moreover, the permanent change in surface tension would allow water-based, solvent-based and UV-based printing technologies to be used.

Figures 1 and 2 below diagram the surface preparation and photografting technique for a polymeric substrate:

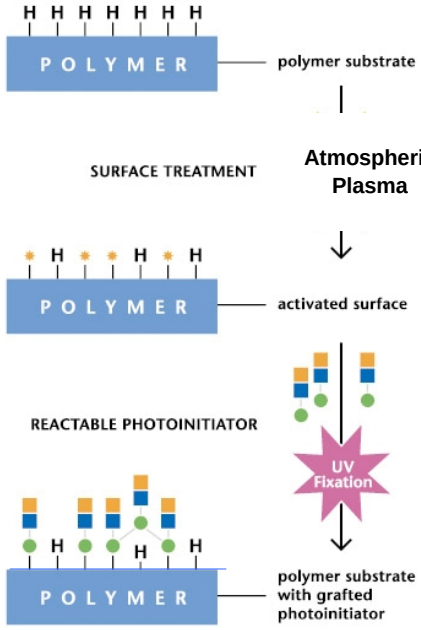


**Figure 1. Plasma-Photografting Process**

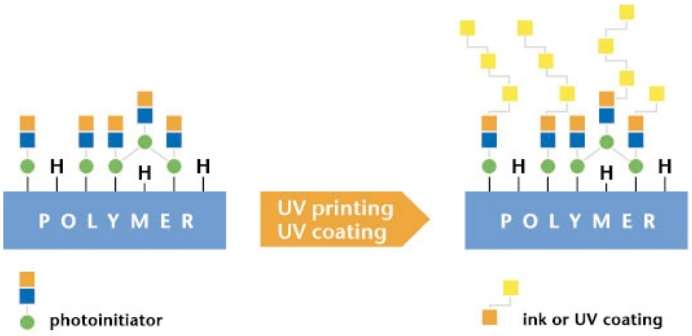


**Figure 2. Post-Photografting Converting Process**

**Experimental Set-Up**

A polypropylene-based substrate was selected for trial. An atmospheric plasma glow discharge treatment station was set at 2.2kW of output power which reacted a mixture of 6.4 liters/min. of helium and 1.6 liters/min. of oxygen for pretreating the three-dimensional polypropylene material. The water-borne photografting solution was applied to the surface of the three dimensional surface with a printing device using an 813 lpi anilox roll, infared/air dried and UV cured. Approximately twenty percent of the photografted surface was

printed with a small solid color block shape using a UV flexo ink to gauge peel adhesion between unprinted and printed surface areas. All treatment devices were integrated into a continuous processing line. Following treatments, peel adhesion data was measured using a Thwing-Albert 180 degree friction peel tester according to ASTM D3330 and PSTC-1,2,3,4 test standards. A cross hatch tape test for ink adhesion was also conducted by ASTM F2452-04.

**Experimental Results**

Several observations can be made from Table 1 and Figure 3. Most notably is the seven-fold increase in peel adhesion between the untreated control sample and the atmospheric plasma-treated sample and nearly eight-fold increase in peel adhesion measured after the photografting process in the untreated areas.

Extended plasma/photografting treatment longevities relative to polypropylene substrates indicate that surface energies are maintained in excess of one year from application. Previous treatment longevity and ink adhesion studies related to the photografting effect on polypropylene film have been conducted by the author and confirm a non-degrading surface tension of 48 dynes/cm over a minimum of a one year period. In addition, ink adhesion tests have confirmed 100% ink retention following tape peel adhesion methods over the same one year period.

| Condition | Area Tested | Mean Peel (grams) | Peak Peel (grams) | Ink Adhesion | Dynes/cm |
|---|---|---|---|---|---|
| Untreated (Control) | Unprinted | 43.3 | 71.3 | n/a | 35 |
| Untreated | Printed | 48.7 | 69.7 | 85% | n/a |
| Plasma-Treated | Unprinted | 311.3 | 452.7 | n/a | 54 |
| Plasma-Treated + Photografting | Unprinted | 339.0 | 443.1 | n/a | 54 |
| Plasma-Treated + Photografting | Printed | 47.2 | 80.5 | 98% | 52 |

**Table 1. Peel Adhesion Data Table**

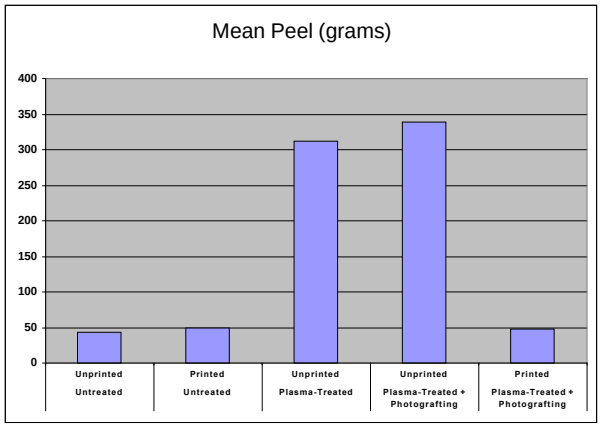


**Figure 3. Peel Adhesion Data Chart**

Although no peel adhesion was gained between the untreated control and UV printed surfaces, confirming that neither the atmospheric plasma functionalities nor the residual photografted molecules became present through interactions with the ink. Both the peel adhesion test and cross hatch test identified approximately a 15% increase in ink adhesion between the printed control sample and the printed plasma/photografted sample.

**Conclusions**

The use of atmospheric plasma glow discharge technology to homogenously microetch, clean and functionalize web surfaces in advance of the uniform surface deposition and fixation of a photografting molecule appears to offer excellent surface adhesion properties for UV flexo inks. Surface energy levels of 52-54 dynes/cm were achieved after both the plasma treating and photografting processes, and the final photografted web polypropylene surface is expected to remain permanently at this surface energy level as indicated by ongoing studies of these materials, and relative to the permanent longevities studied and observed on polymer film materials such as polypropylene, polyester, polyethylene and polyamide previous to this paper. Also noteworthy is that there was no observed change in substrate color or organoleptic measures such as odor following this treatment protocol, nor with regard to the film-based materials studied previously.

**References**

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